Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Why Lanthanide Er^{III} SIMs cannot Possess Huge Energy Barriers: A Theoretical Investigation

Fang Lu, Man-Man Ding, Jia-Xin Li, Bao-Lin Wang, and Yi-Quan Zhang*

Jiangsu Key Lab for NSLSCS, School of Physical Science and Technology, Nanjing Normal University, Nanjing 210023, P. R. China

Table S1. Calculated crystal field parameters of complexes **1**–**3** by CASSCF/RASSI-SO using CASSCF/RASSI-SO with MOLCAS 8.4.

k	*q*	**1**	**2**	**3**
		B(*k*, *q*)		
2	–2	-0.6513×10^{-3}	0.2672	-0.2076×10^{-2}
	–1	0.1693×10^{-1}	0.3437	0.4190×10^{-1}
	0	-0.3052×10^{1}	-0.3713×10^{1}	-0.2132×10^{1}
	1	-0.5389×10^{-1}	0.5334×10^{-1}	-0.2480×10^{-2}
	2	-0.9171×10^{-2}	0.2402	0.2405×10^{-2}
4	–4	0.2965×10^{-3}	0.3783×10^{-2}	0.6064×10^{-4}
	–3	0.6510×10^{-1}	0.1145×10^{-1}	-0.5133×10^{-1}
	–2	-0.2498×10^{-4}	0.4954×10^{-3}	-0.8158×10^{-5}
	–1	-0.4655×10^{-4}	-0.1448×10^{-2}	-0.8354×10^{-4}
	0	0.1269×10^{-2}	0.2681×10^{-2}	-0.7049×10^{-4}
	1	0.2239×10^{-3}	0.3858×10^{-3}	0.8678×10^{-5}
	2	0.6390×10^{-4}	-0.2706×10^{-3}	-0.5762×10^{-4}
	3	-0.2021×10^{-1}	-0.4705×10^{-1}	-0.8118×10^{-2}
	4	0.3105×10^{-5}	0.8271×10^{-3}	-0.2598×10^{-3}
6	–6	0.2040×10^{-3}	0.1379×10^{-3}	0.2399×10^{-3}
	–5	-0.8209×10^{-5}	-0.7424×10^{-4}	0.1021×10^{-4}
	–4	-0.1989×10^{-5}	-0.3237×10^{-4}	-0.1431×10^{-5}
	–3	-0.4566×10^{-3}	0.7310×10^{-4}	0.3960×10^{-3}
	–2	0.2428×10^{-5}	-0.3512×10^{-4}	-0.2054×10^{-5}
	–1	0.3069×10^{-6}	0.3375×10^{-5}	0.4820×10^{-6}
	0	-0.3248×10^{-5}	-0.2872×10^{-4}	0.4245×10^{-5}
	1	-0.2251×10^{-5}	-0.2103×10^{-4}	0.1384×10^{-6}
	2	-0.3013×10^{-5}	0.2323×10^{-4}	0.3327×10^{-5}
	3	0.2399×10^{-3}	0.9674×10^{-4}	0.2589×10^{-3}
	4	0.1024×10^{-5}	-0.3777×10^{-4}	0.1800×10^{-5}
	5	0.1370×10^{-4}	-0.2559×10^{-3}	0.9634×10^{-5}
	6	-0.2288×10^{-3}	0.3759×10^{-4}	-0.2714×10^{-3}

Table S2. Calculated energy levels (cm^{-1}), ***g*** (g_x, g_y, g_z) tensors and predominant m_J values of the lowest eight Kramers doublets (KDs) for **1** with the different included θ angles (degree) keeping the Er-N bond lengths (Å) fixed using CASSCF/RASSI-SO with MOLCAS 8.4.

θ	60°			65°			70°		
KDs	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
1	0.0	0.002 0.003 17.701	±15/2	0.0	0.001 0.001 17.897	±15/2	0.0	0.000 0.000 17.893	±15/2
2	10.5	0.064 0.069 15.063	±13/2	30.0	0.142 0.143 15.367	±13/2	66.2	0.145 0.146 15.454	±13/2
3	82.0	0.328 0.343 11.204	±11/2	114.6	0.211 0.218 12.223	±11/2	155.0	0.161 0.164 12.609	±11/2
4	127.1	0.552 0.571 7.050	±9/2	177.3	0.139 0.150 8.341	±9/2	228.5	0.062 0.069 9.315	±9/2
5	134.8	8.976 7.853 1.683	±1/2	204.8	8.275 7.995 3.054	±5/2	276.9	7.302 7.180 4.495	±7/2
6	253.9	8.317 7.569 1.889	±3/2	320.4	8.099 7.731 1.448	±3/2	387.6	7.207 7.035 2.396	±3/2
7	265.0	0.064 0.780 6.511	±7/2	343.3	0.086 0.541 5.239	±7/2	430.3	0.138 0.377 4.433	±5/2
8	277.5	8.752 7.878 2.319	±5/2	364.2	9.358 8.596 1.229	±1/2	460.8	9.520 8.902 1.030	±1/2
θ	74.8°			80°			85°		
KDs	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
1	0.0	0.000 0.000 17.881	±15/2	0.0	0.000 0.000 17.881	±15/2	0.0	0.000 0.000 17.881	±15/2
2	109.4	0.137 0.137 15.477	±13/2	155.3	0.129 0.129 15.479	±13/2	191.5	0.122 0.122 15.470	±13/2
3	196.6	0.134 0.134 12.803	±11/2	237.9	0.117 0.117 12.927	±11/2	270.3	0.109 0.110 13.000	±11/2
4	272.6	0.024 0.029 9.923	±9/2	310.6	0.024 0.028 10.298	±9/2	338.4	0.019 0.023 10.486	±9/2

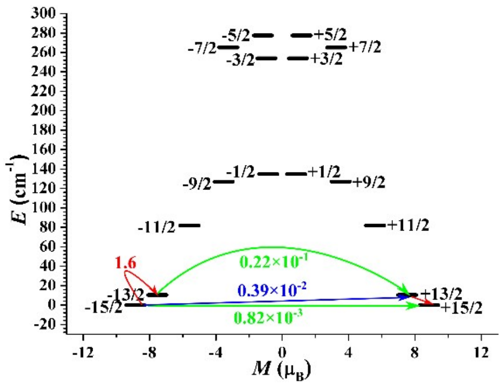
5	338.6	5.988 5.942 5.871	±7/2	390.1	4.628 4.675 6.914	±7/2	425.6	3.919 3.955 7.397	±7/2
6	448.9	5.975 5.879 3.637	±3/2	506.1	4.613 4.648 4.698	±5/2	549.9	3.959 3.988 5.047	±5/2
7	512.5	0.128 0.238 3.957	±5/2	589.6	0.191 0.240 3.676	±3/2	648.3	0.191 0.220 3.549	±3/2
8	553.0	9.556 9.146 1.058	±1/2	640.9	9.673 9.217 1.109	±1/2	708.7	9.704 9.282 1.136	±1/2

θ / KDs	90°		
	E/cm^{-1}	***g***	m_J
1	0.0	0.000 0.000 17.866	±15/2
2	212.6	0.113 0.113 15.455	±13/2
3	291.6	0.102 0.103 13.039	±11/2
4	358.2	0.013 0.017 10.565	±9/2
5	448.2	3.874 3.900 7.489	±7/2
6	579.9	3.891 3.920 5.093	±5/2
7	686.8	0.159 0.208 3.526	±3/2
8	753.0	9.697 9.323 1.140	±1/2

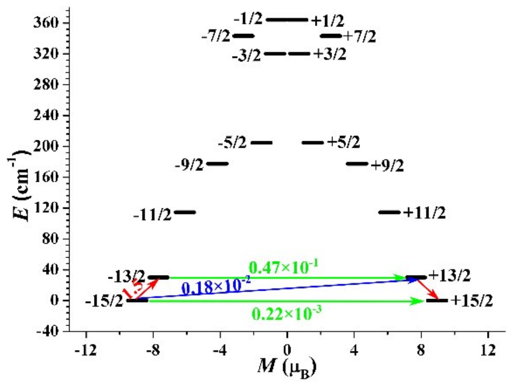
Table S3. Wave functions with definite projection of the total moments | m_J > for the lowest two KDs for **1** with the different included θ angles (degree) keeping the Er-N bond lengths (Å) fixed using CASSCF/RASSI-SO with MOLCAS 8.4.

θ	E/cm^{-1}	wave functions
60°	0.0	97.45%|±15/2>+2.08%|±9/2>

	10.5	94.59%|±13/2>+4.36%|±7/2>
65°	0.0	99.82%|±15/2>
	30.0	99.22%|±13/2>
70°	0.0	99.75%|±15/2>
	66.2	99.34%|±13/2>
74.8°	0.0	99.59%|±15/2>
	109.4	99.69%|±13/2>
80°	0.0	99.61%|±15/2>
	155.3	99.77%|±13/2>
85°	0.0	99.62%|±15/2>
	191.5	99.70%|±13/2>
90°	0.0	99.42%|±15/2>
	212.6	99.53%|±13/2>



60°



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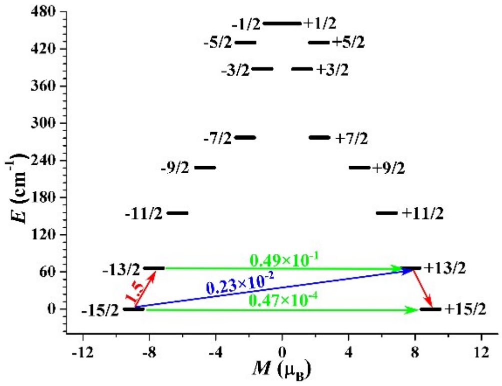

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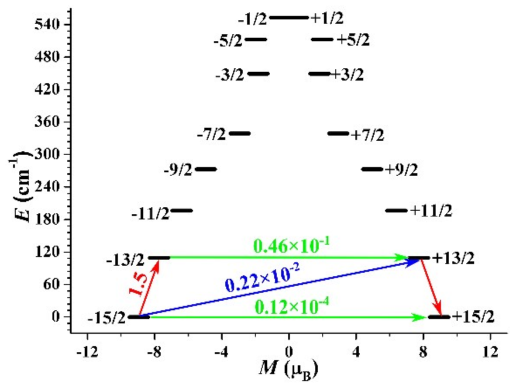

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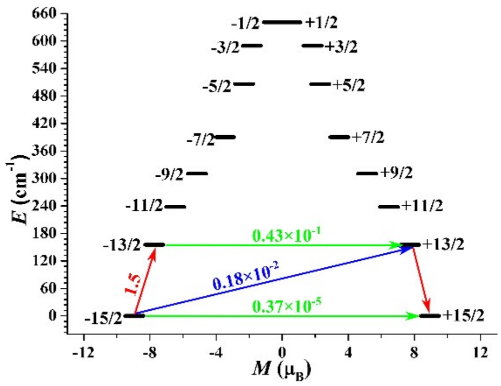

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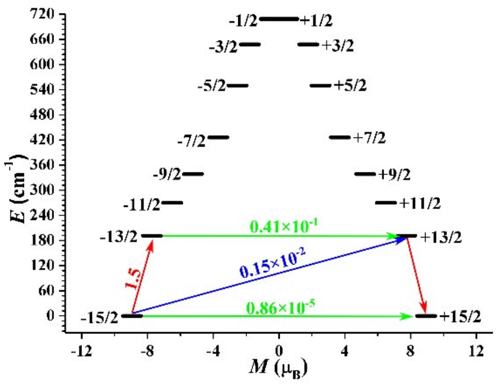
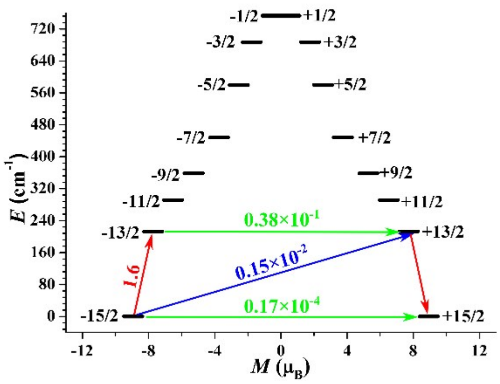


85°



90°

Figure S1. Magnetization blocking barriers for **1** with the different included θ angles keeping Er-N bond lengths fixed. The thick black lines represent the KDs as a function of their magnetic moments along the magnetic axes. The green lines correspond to diagonal matrix elements of their transversal magnetic moments; the blue lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S4. Calculated energy levels (cm^{-1}), $\boldsymbol{g}$ (g_x, g_y, g_z) tensors and predominant m_J values of the lowest eight KDs for **2** with the different included θ angles (degree) keeping the Er-O bond lengths (Å) fixed using CASSCF/RASSI-SO with MOLCAS 8.4[1].

θ / KDs	60°			65°			70°		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.005 0.006 17.845	±15/2	0.0	0.001 0.001 17.891	±15/2	0.0	0.001 0.001 17.895	±15/2
2	84.4	0.073 0.087 15.196	±13/2	114.1	0.023 0.031 15.360	±13/2	143.5	0.012 0.017 15.411	±13/2
3	151.9	0.004 0.027 12.254	±11/2	187.6	0.027 0.036 12.644	±11/2	220.5	0.015 0.036 12.860	±11/2
4	211.2	1.879	±9/2	254.4	1.186	±9/2	291.9	0.760	±9/2

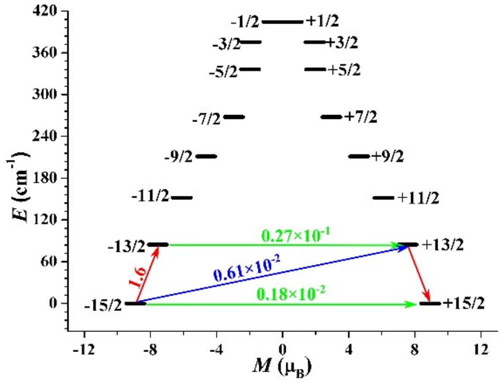
		1.989 9.266			1.191 9.968			0.777 10.355	
5	267.7	6.991 5.808 3.292	±7/2	325.6	2.587 4.835 7.098	±7/2	375.7	2.081 3.555 7.702	±7/2
6	336.2	2.649 3.907 7.377	±5/2	406.9	5.894 4.849 1.517	±5/2	471.0	5.337 4.970 0.722	±5/2
7	375.5	1.806 4.488 8.636	±3/2	464.8	2.036 3.946 7.853	±3/2	545.8	2.326 3.559 7.571	±3/2
8	404.3	0.668 3.210 14.696	±1/2	504.6	0.808 3.923 14.372	±1/2	597.0	0.854 4.167 14.302	±1/2
θ	75.7°			80°			85°		
KDs	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.001 0.001 17.887	±15/2	0.0	0.001 0.001 17.879	±15/2	0.0	0.000 0.000 17.868	±15/2
2	167.7	0.019 0.021 15.427	±13/2	176.1	0.024 0.026 15.439	±13/2	181.7	0.028 0.030 15.463	±13/2
3	248.1	0.001 0.031 13.000	±11/2	259.9	0.003 0.036 13.063	±11/2	261.4	0.011 0.037 13.093	±11/2
4	323.6	0.467 0.496 10.580	±9/2	339.8	0.356 0.392 10.667	±9/2	349.0	0.275 0.312 10.700	±9/2
5	418.6	2.028 2.952 7.976	±7/2	440.8	2.138 2.832 8.031	±7/2	454.2	2.307 2.820 7.999	±7/2
6	527.9	5.496 4.704 0.369	±5/2	557.2	5.487 4.791 0.305	±5/2	573.9	5.440 4.955 0.298	±5/2
7	618.0	2.204 3.245 7.009	±3/2	653.3	2.888 3.138 8.052	±3/2	671.9	2.891 3.258 8.570	±3/2
8	677.7	0.921 4.747 13.889	±1/2	723.2	0.804 3.772 14.671	±1/2	746.3	0.740 3.350 14.972	±1/2

θ	90°		
KDs	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.001 0.001	±15/2

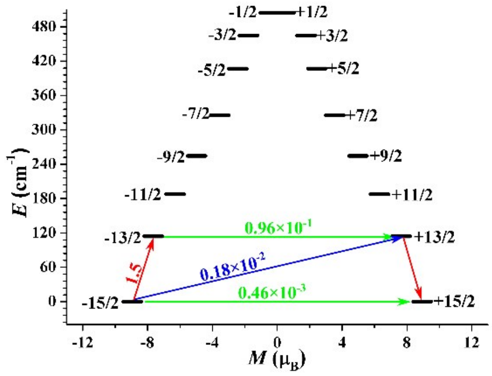
		17.862	
2	193.9	0.033 0.034 15.493	±13/2
3	251.1	0.023 0.034 13.085	±11/2
4	352.1	0.267 0.294 10.659	±9/2
5	454.8	2.405 2.863 7.896	±7/2
6	572.0	5.4360 5.0334 0.2783	±5/2
7	666.0	2.737 3.483 9.104	±3/2
8	740.5	0.670 2.928 15.245	±1/2

Table S5. Wave functions with definite projection of the total moments | m_J > for the lowest two KDs for **2** with the different included θ angles (degree) keeping the Er-O bond lengths (Å) fixed using CASSCF/RASSI-SO with MOLCAS 8.4.

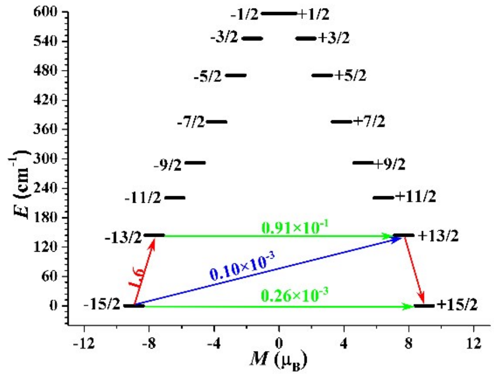
θ	E/cm^{-1}	wave functions
60°	0.0	98.87%|±15/2>
	84.4	92.68%|±13/2>+4.05%|±7/2>
65°	0.0	99.62%|±15/2>
	114.1	95.81%|±13/2>+2.13%|±7/2>
70°	0.0	99.74%|±15/2>
	143.5	97.64%|±13/2>
75.7°	0.0	99.71%|±15/2>
	167.7	98.82%|±13/2>
80°	0.0	99.60%|±15/2>
	176.1	99.18%|±13/2>
85°	0.0	99.46%|±15/2>
	181.7	99.24%|±13/2>
90°	0.0	99.40%|±15/2>
	193.9	99.07%|±13/2>



60°



65°



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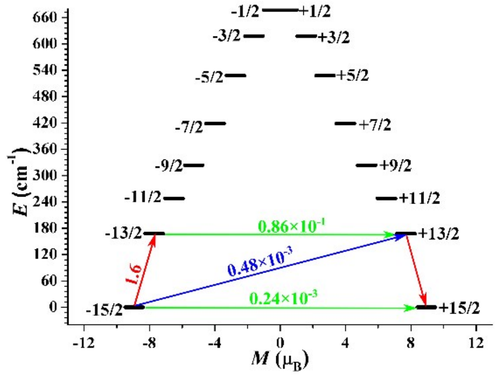
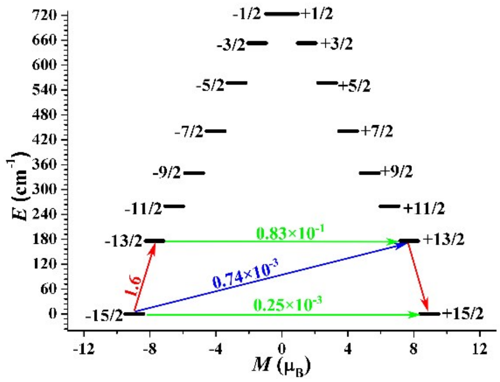
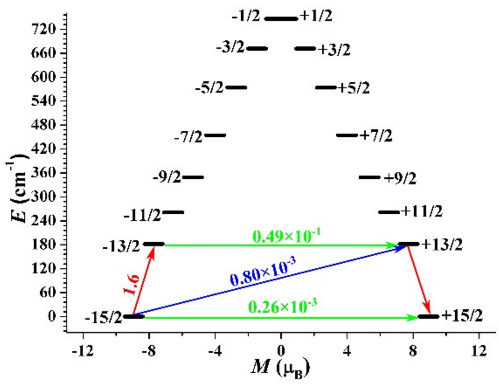


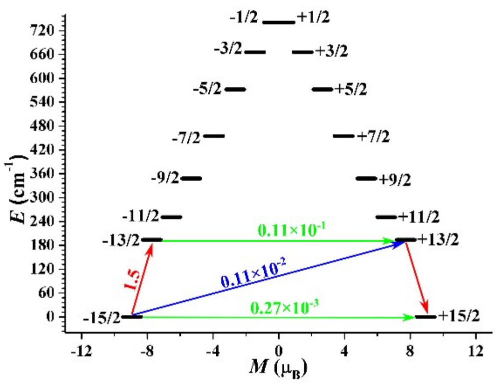
75.7°



80°



85°



90°

Figure S2. Magnetization blocking barriers for **2** with the different included θ angles keeping the Er-O bond lengths fixed. The thick black lines represent the KDs as a function of their magnetic moments along the magnetic axes. The green lines correspond to diagonal matrix elements of their transversal magnetic moments; the blue lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S6. Calculated energy levels (cm^{-1}), $\boldsymbol{g}$ (g_x, g_y, g_z) tensors and predominant m_J values of the lowest eight KDs for **3** with the different included θ angles (degree) keeping the Er-C bond lengths (Å) fixed using CASSCF/RASSI-SO with MOLCAS 8.4[1].

θ	60°			65°			69.3°		
KDs	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.001 0.001 17.765	±15/2	0.0	0.000 0.000 17.789	±15/2	0.0	0.000 0.000 17.819	±15/2
2	16.7	0.320 0.323 15.280	±13/2	49.4	0.294 0.295 15.375	±13/2	81.6	0.293 0.293 15.406	±13/2
3	73.5	0.280 0.287 11.728	±11/2	117.9	0.165 0.169 12.472	±11/2	155.7	0.185 0.186 12.702	±11/2
4	92.5	8.927 8.803 1.821	±1/2	160.6	0.037 0.054 8.325	±9/2	208.4	0.019 0.030 9.193	±9/2
5	97.8	0.052 0.072 6.882	±9/2	169.5	8.705 8.600 2.820	±5/2	232.1	8.290 8.230 3.665	±5/2
6	207.4	6.092 5.568 3.874	±3/2	289.9	8.334 7.976 1.492	±1/2	353.3	8.180 8.006 1.429	±3/2
7	212.4	0.109 0.398 6.379	±7/2	297.7	0.032 0.409 4.813	±7/2	372.7	0.046 0.243 3.979	±7/2
8	216.9	5.779 5.502 4.475	±5/2	305.9	9.055 8.575 1.749	±3/2	389.0	9.415 9.076 1.037	±1/2
θ	75°			80°			85°		
KDs	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.000 0.000 17.871	±15/2	0.0	0.000 0.000 17.907	±15/2	0.0	0.000 0.000 17.920	±15/2
2	126.6	0.284 0.284	±13/2	162.7	0.268 0.268	±13/2	192.1	0.246 0.246	±13/2

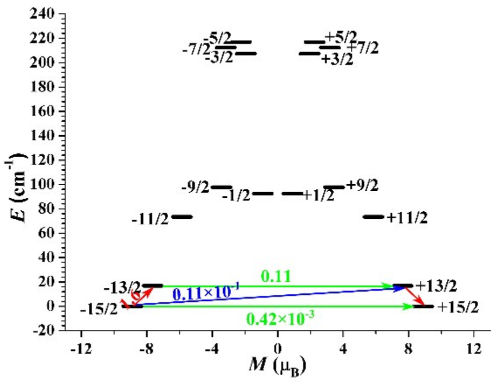
		15.437			15.458			15.465	
3	204.2	0.205 0.207 12.866	±11/2	242.4	0.210 0.212 12.946	±11/2	274.9	0.202 0.203 12.996	±11/2
4	263.7	0.007 0.019 9.881	±9/2	304.3	0.005 0.015 10.191	±9/2	339.0	0.004 0.013 10.356	±9/2
5	307.6	7.582 7.549 4.810	±7/2	363.1	6.940 6.914 5.609	±7/2	408.7	6.422 6.400 6.131	±7/2
6	432.0	7.539 7.459 2.421	±3/2	492.6	6.930 6.872 3.221	±3/2	543.5	6.425 6.379 3.740	±5/2
7	470.7	0.057 0.135 3.428	±5/2	547.8	0.066 0.108 3.253	±5/2	612.2	0.072 0.096 3.214	±3/2
8	498.5	9.516 9.293 1.011	±1/2	584.9	9.575 9.376 1.067	±1/2	657.2	9.605 9.414 1.101	±1/2

θ / KDs	90°		
	E/cm^{-1}	***g***	m_J
1	0.0	0.000 0.000 17.908	±15/2
2	211.3	0.220 0.220 15.457	±13/2
3	299.7	0.182 0.183 13.025	±11/2
4	367.7	0.006 0.013 10.438	±9/2
5	443.6	6.096 6.119 6.391	±7/2
6	582.0	6.123 6.081 3.974	±5/2
7	659.5	0.079 0.099 3.247	±3/2
8	710.0	9.621 9.420	±1/2

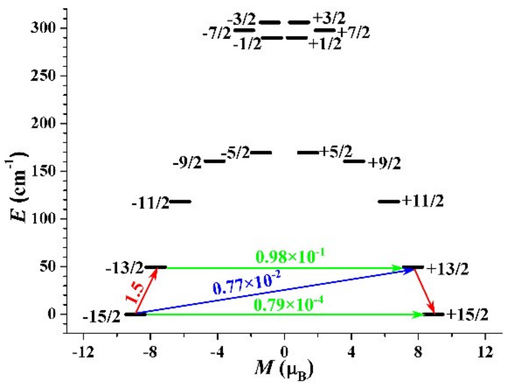
		1.111	

Table S7. Wave functions with definite projection of the total moments | m_J > for the lowest two KDs for **3** with the different included θ angles (degree) keeping the Er-C bond lengths (Å) fixed using CASSCF/RASSI-SO with MOLCAS 8.4.

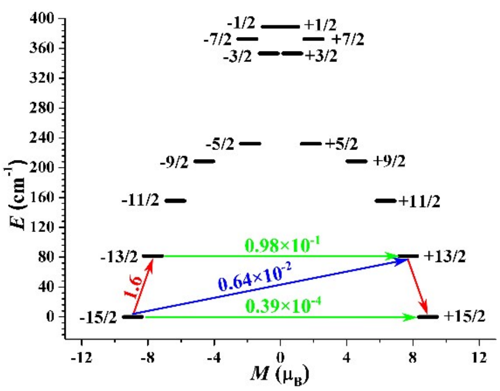
θ	E/cm^{-1}	wave functions
60°	0.0	98.24%|±15/2>
	16.7	97.52%|±13/2>
65°	0.0	98.36%|±15/2>
	49.4	98.64%|±13/2>
69.3°	0.0	98.66%|±15/2>
	81.6	98.99%|±13/2>
75°	0.0	99.31%|±15/2>
	126.6	99.33%|±13/2>
80°	0.0	99.78%|±15/2>
	162.7	99.57%|±13/2>
85°	0.0	99.96%|±15/2>
	192.1	99.65%|±13/2>
90°	0.0	99.80%|±15/2>
	211.3	99.52%|±13/2>



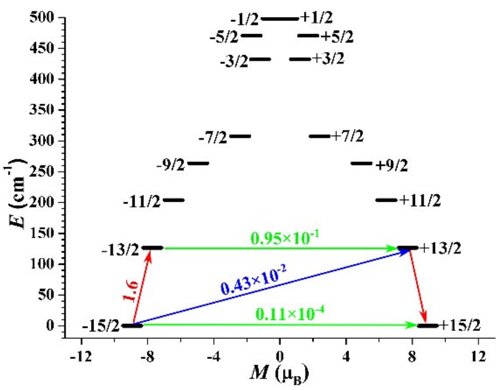
60°



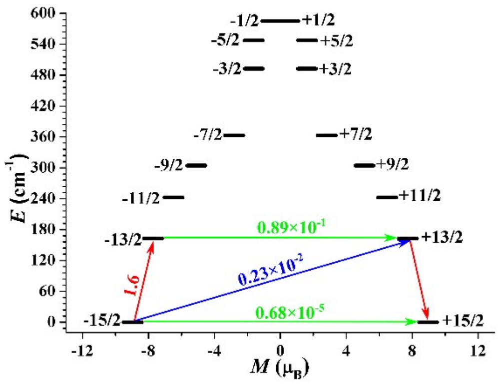
65°



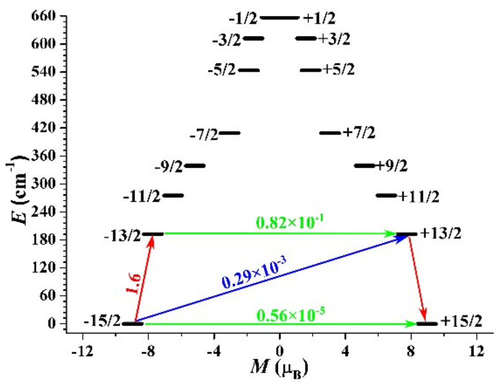
69.3°



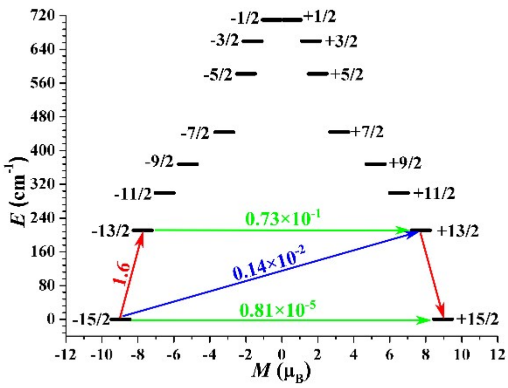
75°



80°



85°



90°

Figure S3. Magnetization blocking barriers for **3** with the different included θ angles keeping the Er-C bond lengths fixed. The thick black lines represent the KDs as a function of their magnetic moments along the magnetic axes. The green lines correspond to diagonal matrix elements of their transversal magnetic moments; the blue lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S8. Calculated energy levels (cm^{-1}), $\boldsymbol{g}$ (g_x, g_y, g_z) tensors and predominant m_J values of the lowest eight KDs for simple model $Er(NH_2)_3$ with the different included θ angles (degree) keeping the Er-N bond lengths (Å) fixed using CASSCF/RASSI-SO with MOLCAS 8.4.

θ / KDs	40°			50°			60°		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.015 0.021 14.423	±15/2	0.0	0.000 0.001 17.062	±15/2	0.0	0.000 0.000 17.826	±15/2
2	19.3	6.918 6.912 5.366	±7/2	39.5	0.479 0.480 14.507	±13/2	52.7	0.018 0.019 15.394	±13/2
3	57.3	5.823 5.787 0.115	±3/2	116.2	0.259 0.266 11.323	±11/2	159.2	0.047 0.049 12.672	±11/2
4	75.9	0.013	±5/2	151.5	9.443	±1/2	246.1	0.055	±9/2

		0.019 4.434			8.918 1.323			0.062 9.245	
5	104.8	7.700 7.617 0.127	±1/2	163.3	0.236 0.264 5.682	±7/2	284.4	8.079 7.979 3.684	±5/2
6	188.0	1.770 1.781 11.106	±9/2	232.1	6.780 6.366 3.856	±3/2	378.8	7.909 7.555 1.587	±3/2
7	229.5	0.016 0.045 13.075	±13/2	241.9	0.055 0.363 8.901	±9/2	395.6	0.069 0.503 4.847	±7/2
8	241.4	2.206 2.281 11.954	±11/2	256.4	6.788 6.517 5.325	±5/2	413.7	9.532 8.862 1.163	±1/2

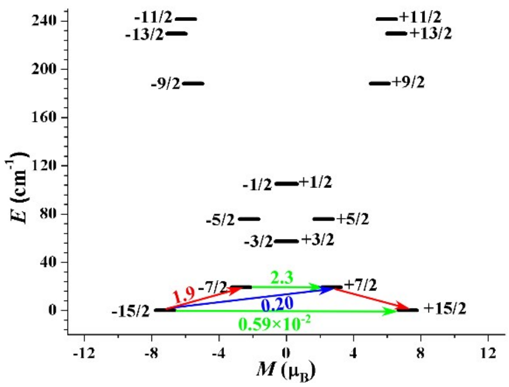
θ / KDs	70°			74.8°			80°		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.000 0.000 17.858	±15/2	0.0	0.000 0.000 17.829	±15/2	0.0	0.000 0.000 17.860	±15/2
2	103.4	0.049 0.049 15.484	±13/2	118.0	0.174 0.174 15.457	±13/2	215.6	0.076 0.076 15.484	±13/2
3	239.3	0.063 0.063 12.901	±11/2	225.6	0.154 0.155 12.843	±11/2	309.1	0.079 0.079 12.978	±11/2
4	331.8	0.020 0.025 10.117	±9/2	321.8	0.019 0.024 10.011	±9/2	388.3	0.013 0.016 10.424	±9/2
5	407.5	5.631 5.664 6.160	±7/2	399.4	5.622 5.662 6.043	±7/2	484.1	3.766 3.789 7.323	±7/2
6	523.1	5.582 5.516 3.862	±3/2	517.3	5.695 5.625 3.734	±3/2	624.1	3.760 3.788 5.004	±5/2
7	593.8	0.128 0.238 4.042	±5/2	592.0	0.117 0.186 3.831	±5/2	739.2	0.134 0.189 3.722	±3/2
8	638.8	9.613 9.203 1.093	±1/2	640.1	9.518 9.177 1.050	±1/2	809.7	9.648 9.310 1.132	±1/2

θ / KDs	90°		
	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.000 0.000	±15/2

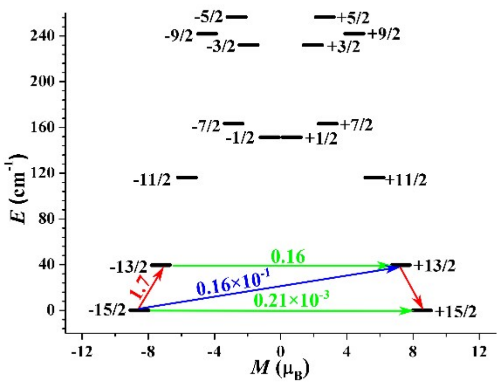
		17.859	
2	233.7	0.108 0.108 15.478	±13/2
3	322.6	0.098 0.099 12.983	±11/2
4	398.2	0.012 0.015 0.460	±9/2
5	499.4	3.119 3.143 7.561	±7/2
6	644.8	3.175 3.195 5.238	±5/2
7	772.1	0.141 0.174 3.632	±3/2
8	850.1	9.641 9.315 1.135	±1/2

Table S9. Wave functions with definite projection of the total moments | m_J > for the lowest two KDs for simple model $Er(NH_2)_3$ with the different included θ angles (degree) keeping the Er-N bond lengths (Å) fixed using CASSCF/RASSI-SO with MOLCAS 8.4.

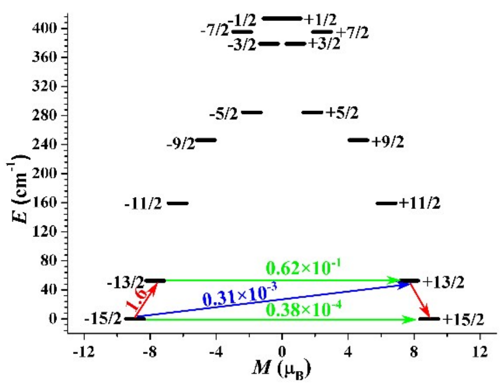
θ	E/cm^{-1}	wave functions
40°	0.0	56.95%|±15/2>+37.72%|±9/2>
	19.3	12.21%|±13/2>+40.00%|±7/2>+41.11%|±1/2>+6.43%|±5/2>
50°	0.0	88.44%|±15/2>+11.02%|±9/2>
	39.5	86.59%|±13/2>+12.56%|±7/2>
60°	0.0	98.71%|±15/2>
	52.7	98.27%|±13/2>
70°	0.0	99.20%|±15/2>
	103.4	99.67%|±13/2>
74.8°	0.0	98.85%|±15/2>
	118.0	99.50%|±13/2>
80°	0.0	99.29%|±15/2>
	215.6	99.87%|±13/2>
90°	0.0	99.30%|±15/2>
	233.7	99.84%|±13/2>



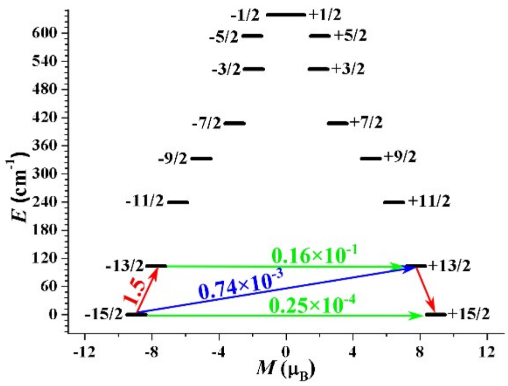
40°



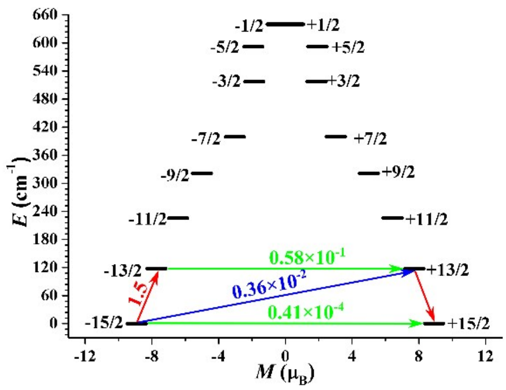
50°



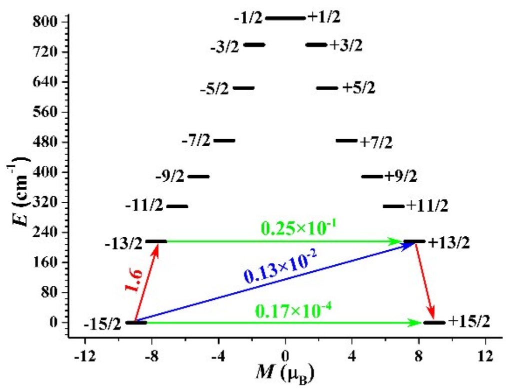
60°



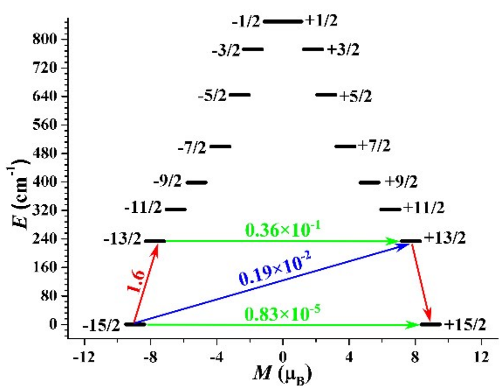
70°



74.8°



80°



90°

Figure S4. Magnetization blocking barriers for simple model $Er(NH_2)_3$ with the different included θ angles keeping the Er-N bond lengths fixed. The thick black lines represent the KDs as a function of their magnetic moments along the magnetic axes. The green lines correspond to diagonal matrix elements of their transversal magnetic moments; the blue lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S10. Calculated energy levels (cm^{-1}), ***g*** (g_x, g_y, g_z) tensors and predominant m_J values of the lowest eight KDs for **1** with the different Er-N bond lengths (Å) keeping the θ of 90° using CASSCF/RASSI-SO with MOLCAS 8.4.

Er-N \ KDs	1.80 Å			1.90 Å			2.00 Å		
	E/cm^{-1}	***g***	m_J	*E*/cm^{-1}	***g***	m_J	*E*/cm^{-1}	***g***	m_J
1	0.0	0.005 0.013 15.068	±15/2	0.0	0.036 0.063 17.009	±15/2	0.0	0.000 0.000 17.702	±15/2
2	121.7	7.021 6.987 5.302	±7/2	194.6	1.204 4.506 10.944	±9/2	241.3	0.302 0.303 15.246	±13/2
3	170.8	0.018 0.062 12.125	±11/2	207.3	0.669 3.423 11.914	±7/2	283.2	0.285 0.287 12.935	±11/2
4	179.5	1.697 1.740 11.706	±9/2	236.3	0.894 4.276 11.043	±13/2	320.5	0.010 0.017 10.570	±9/2
5	266.1	1.522 1.531 13.713	±13/2	294.8	1.920 3.592 12.344	±11/2	404.2	4.223 4.245 7.378	±7/2
6	452.5	7.371 7.288 2.316	±3/2	487.8	3.241 4.287 8.600	±3/2	568.3	4.258 4.305 4.888	±5/2
7	597.0	0.037 0.181 3.366	±5/2	643.6	3.603 2.788 1.490	±5/2	710.0	0.066 0.149 3.602	±3/2
8	705.1	9.397 9.175 0.891	±1/2	746.5	9.876 8.902 1.024	±1/2	800.7	9.585 9.370 1.130	±1/2
Er-N \ KDs	2.10 Å			2.20 Å			2.30 Å		
	E/cm^{-1}	***g***	m_J	*E*/cm^{-1}	***g***	m_J	*E*/cm^{-1}	***g***	m_J
1	0.0	0.000 0.000 17.810	±15/2	0.0	0.000 0.000 17.862	±15/2	0.0	0.000 0.000 17.892	±15/2
2	230.8	0.155 0.155 15.398	±13/2	214.5	0.116 0.116 15.451	±13/2	196.7	0.093 0.093 15.480	±13/2
3	295.4	0.147	±11/2	292.5	0.105	±11/2	281.6	0.081	±11/2

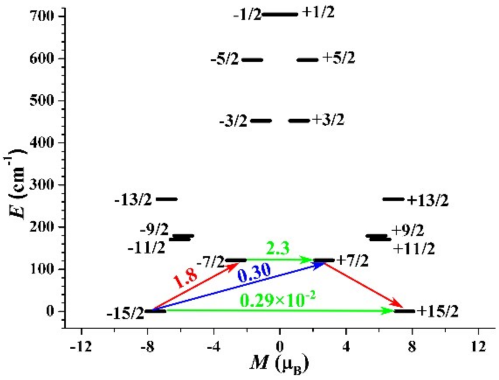
		0.148 13.003			0.106 13.036			0.082 13.058	
4	350.4	0.008 0.014 10.564	±9/2	358.3	0.008 0.013 10.564	±9/2	353.4	0.009 0.012 10.572	±9/2
5	440.6	3.778 3.796 7.515	±7/2	448.4	3.863 3.881 7.493	±7/2	440.8	3.980 3.998 7.467	±7/2
6	586.8	3.788 3.822 5.108	±5/2	581.5	3.877 3.903 5.097	±5/2	561.4	3.998 4.017 5.070	±5/2
7	712.1	0.076 0.140 3.563	±3/2	690.2	0.084 0.134 3.528	±3/2	655.4	0.090 0.131 3.509	±3/2
8	790.7	9.605 9.390 1.140	±1/2	757.5	9.619 9.400 1.141	±1/2	713.0	9.630 9.408 1.141	±1/2
Er-N	2.40 Å			2.50 Å			2.60 Å		
KDs	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.000 0.000 17.910	±15/2	0.0	0.000 0.000 17.923	±15/2	0.0	0.000 0.000 17.932	±15/2
2	179.3	0.076 0.076 15.498	±13/2	163.1	0.062 0.062 15.512	±13/2	148.6	0.050 0.050 15.521	±13/2
3	267.1	0.064 0.065 13.076	±11/2	251.2	0.050 0.051 13.090	±11/2	235.2	0.039 0.040 13.102	±11/2
4	341.5	0.008 0.012 10.587	±9/2	326.0	0.008 0.011 10.605	±9/2	309.0	0.008 0.010 10.624	±9/2
5	425.1	4.013 4.030 7.474	±7/2	405.2	3.968 3.984 7.512	±7/2	383.8	3.866 3.880 7.569	±7/2
6	533.5	4.031 4.046 5.074	±5/2	502.4	3.985 3.997 5.109	±5/2	470.7	3.881 3.892 5.166	±5/2
7	615.1	0.096 0.129 3.501	±3/2	573.6	0.102 0.130 3.501	±3/2	533.3	0.106 0.130 3.506	±3/2
8	664.5	9.640 9.414 1.143	±1/2	616.2	9.651 9.418 1.146	±1/2	570.3	9.660 9.422 1.151	±1/2
Er-N	2.70 Å								

KDs	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.000 0.000 17.939	±15/2
2	135.8	0.040 0.040 15.529	±13/2
3	220.0	0.031 0.032 13.113	±11/2
4	291.8	0.007 0.009 10.6431	±9/2
5	362.1	3.725 3.738 7.638	±7/2
6	440.1	3.738 3.748 5.234	±5/2
7	495.5	0.109 0.130 3.513	±3/2
8	527.8	9.668 9.426 1.156	±1/2

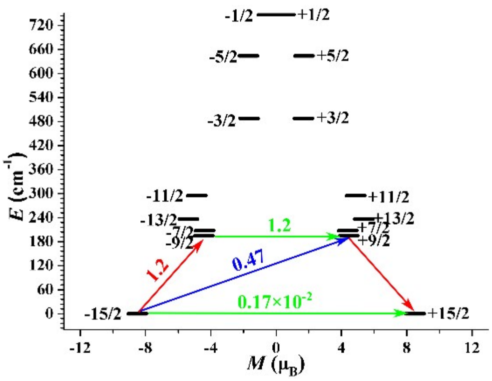
Table S11. Wave functions with definite projection of the total moments $| m_J >$ for the lowest two KDs for **1** with the different Er-N bond lengths (Å) keeping the θ of 90°using CASSCF/RASSI-SO with MOLCAS 8.4.

<table>
<tr><th>θ</th><th>E/cm⁻¹</th><th>wave functions</th></tr>
<tr><td rowspan="2">1.80 Å</td><td>0.0</td><td>66.66%|±15/2>+30.06%|±9/2></td></tr>
<tr><td>121.7</td><td>64.87%|±7/2>+19.66%|±5/2>+7.13%|±1/2>+7.45%|±13/2></td></tr>
<tr><td rowspan="2">1.90 Å</td><td>0.0</td><td>88.28%|±15/2>+9.56%|±9/2></td></tr>
<tr><td>194.6</td><td>17.80%|±13/2>+26.03%|±11/2>+29.00%|±9/2>+14.38%|±7/2>+5.30%|±5/2></td></tr>
<tr><td rowspan="2">2.00 Å</td><td>0.0</td><td>97.86%|±15/2></td></tr>
<tr><td>241.3</td><td>97.57%|±13/2></td></tr>
<tr><td rowspan="2">2.10 Å</td><td>0.0</td><td>98.95%|±15/2></td></tr>
<tr><td>230.8</td><td>99.07%|±13/2></td></tr>
<tr><td rowspan="2">2.20 Å</td><td>0.0</td><td>99.40%|±15/2></td></tr>
<tr><td>214.5</td><td>99.52%|±13/2></td></tr>
<tr><td rowspan="2">2.30 Å</td><td>0.0</td><td>99.61%|±15/2></td></tr>
<tr><td>196.7</td><td>99.69%|±13/2></td></tr>
<tr><td rowspan="2">2.40 Å</td><td>0.0</td><td>99.74%|±15/2></td></tr>
<tr><td>179.3</td><td>99.79%|±13/2></td></tr>
</table>

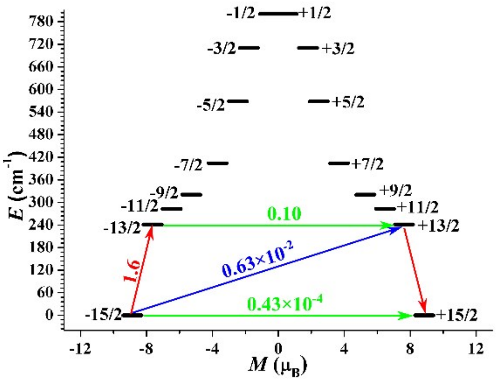
2.50 Å	0.0	99.82%|±15/2>
	163.1	99.84%|±13/2>
2.60 Å	0.0	99.87%|±15/2>
	148.6	99.88%|±13/2>
2.70 Å	0.0	99.90%|±15/2>
	135.8	99.91%|±13/2>



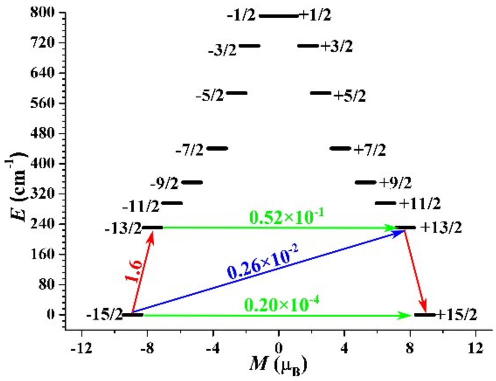
1.80 Å



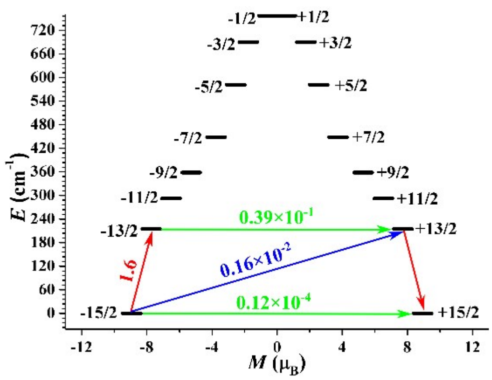
1.90 Å



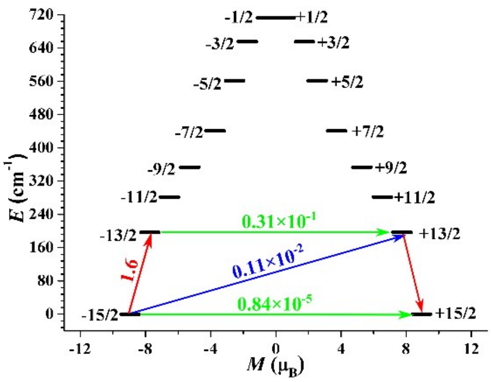
2.00 Å



2.10 Å



2.20 Å



2.30 Å

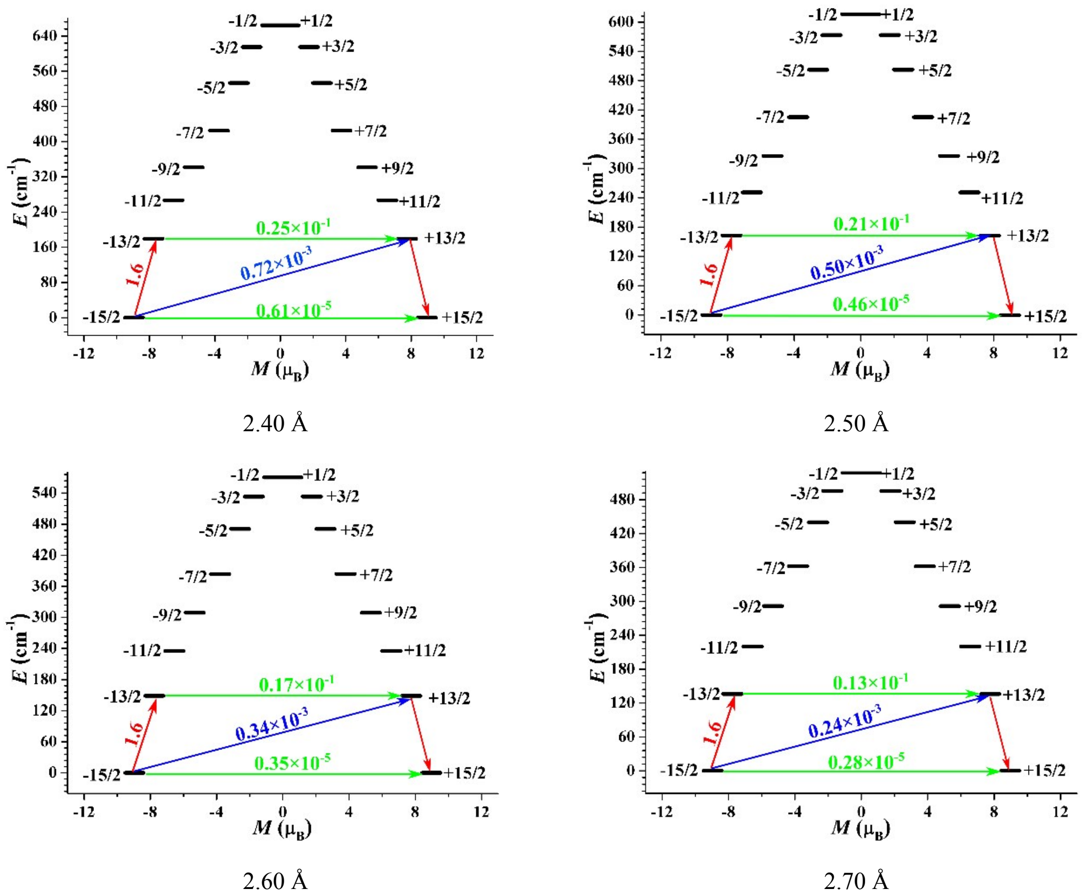


Figure S5. Magnetization blocking barriers for **1** with the different Er-N bond lengths keeping the θ of 90°. The thick black lines represent the KDs as a function of their magnetic moments along the magnetic axes. The green lines correspond to diagonal matrix elements of their transversal magnetic moments; the blue lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S12. Calculated energy levels (cm^{-1}), $\boldsymbol{g}$ (g_x, g_y, g_z) tensors and predominant m_J values of the lowest eight KDs of **2** with the different Er-O bond lengths (Å) keeping the θ of 90°using CASSCF/RASSI-SO with MOLCAS 8.4.

Er-O / KDs	1.80 Å			1.90 Å			2.00 Å		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.083 0.210 17.177	±15/2	0.0	0.008 0.016 17.724	±15/2	0.0	0.001 0.002 17.840	±15/2
2	112.4	2.183 3.269 13.574	±13/2	142.4	0.281 0.316 15.436	±13/2	153.2	0.058 0.061 15.487	±13/2
3	139.9	2.312 2.996 11.211	±11/2	211.5	0.242 0.303 12.977	±11/2	244.9	0.045 0.057 13.071	±11/2
4	196.0	0.882 1.016	±9/2	293.2	0.450 0.514	±9/2	339.3	0.297 0.326	±9/2

		10.775			10.536			10.639	
5	261.8	5.242 5.829 8.022	±7/2	391.6	4.731 5.594 6.867	±7/2	446.0	2.981 3.507 7.711	±7/2
6	497.7	2.509 2.671 11.332	±5/2	550.7	1.734 4.047 8.858	±5/2	571.6	6.212 5.028 0.508	±5/2
7	625.3	1.644 2.056 11.002	±3/2	666.4	2.236 2.579 10.111	±3/2	672.9	2.644 3.016 9.274	±3/2
8	735.4	0.550 2.564 15.301	±1/2	758.7	0.640 2.918 15.197	±1/2	750.6	0.692 3.119 15.096	±1/2
Er-O \ KDs	2.10 Å			2.20 Å			2.30 Å		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.000 0.000 17.888	±15/2	0.0	0.000 0.000 17.914	±15/2	0.0	0.000 0.000 17.929	±15/2
2	152.5	0.017 0.018 15.506	±13/2	145.9	0.008 0.009 15.519	±13/2	136.6	0.006 0.006 15.529	±13/2
3	254.3	0.012 0.017 13.102	±11/2	250.5	0.004 0.010 13.116	±11/2	240.0	0.002 0.007 13.125	±11/2
4	353.2	0.218 0.235 10.681	±9/2	349.0	0.187 0.198 10.697	±9/2	335.2	0.170 0.177 10.706	±9/2
5	457.8	1.957 2.323 8.030	±7/2	447.9	1.639 1.944 8.120	±7/2	427.1	1.533 1.803 8.157	±7/2
6	566.4	5.493 4.407 0.027	±5/2	544.2	5.609 3.575 0.051	±5/2	512.9	5.668 3.079 0.265	±5/2
7	653.2	2.827 3.474 8.656	±3/2	618.4	2.904 3.906 8.238	±3/2	576.6	2.938 4.294 7.969	±3/2
8	719.1	0.712 3.180 15.066	±1/2	674.8	0.713 3.152 15.094	±1/2	625.3	0.705 3.068 15.161	±1/2
Er-O \ KDs	2.40 Å			2.50 Å			2.60 Å		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.000 0.000 17.939	±15/2	0.0	0.000 0.000 17.946	±15/2	0.0	0.000 0.000 17.950	±15/2

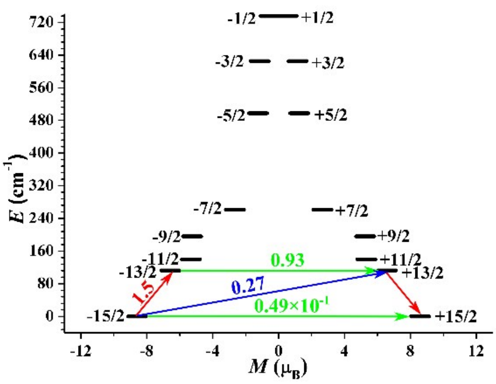
2	126.6	0.004 0.004 15.536	±13/2	116.6	0.003 0.003 15.541	±13/2	107.2	0.002 0.002 15.545	±13/2
3	226.0	0.001 0.005 13.132	±11/2	210.9	0.000 0.004 13.137	±11/2	195.8	0.000 0.003 13.141	±11/2
4	316.6	0.155 0.160 10.714	±9/2	296.0	0.139 0.142 10.721	±9/2	275.2	0.123 0.125 10.727	±9/2
5	401.3	1.424 1.663 8.187	±7/2	373.8	1.282 1.492 8.217	±7/2	346.3	1.121 1.304 8.243	±7/2
6	477.7	0.414 2.668 5.712	±5/2	441.8	0.487 2.281 5.749	±5/2	407.1	0.513 1.910 5.779	±5/2
7	532.9	2.949 4.645 7.802	±3/2	489.9	2.946 4.966 7.702	±3/2	449.4	2.932 5.272 7.649	±3/2
8	575.4	0.689 2.950 15.252	±1/2	527.5	0.670 2.811 15.356	±1/2	482.8	0.646 2.656 15.471	±1/2

Er-O / KDs	2.70 Å		
	E/cm^{-1}	***g***	m_J
1	0.0	0.000 0.000 17.954	±15/2
2	98.6	0.002 0.002 15.549	±13/2
3	181.3	0.001 0.003 13.144	±11/2
4	255.0	0.107 0.109 10.732	±9/2
5	320.0	0.953 1.112 8.266	±7/2
6	374.4	0.511 1.557 5.801	±5/2
7	411.8	7.627 5.568 2.910	±3/2

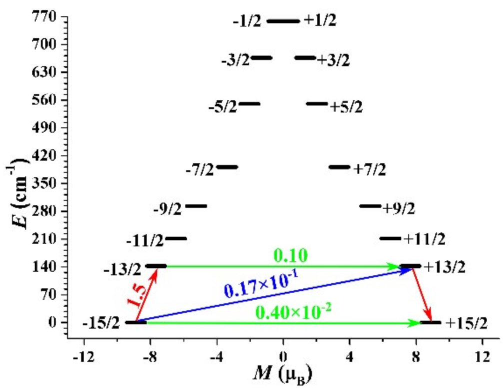
8	441.9	0.619 2.488 15.595	±1/2

Table S13. Wave functions with definite projection of the total moments | m_J > for the lowest two KDs for **2** with the different Er-O bond lengths (Å) keeping the θ of 90°using CASSCF/RASSI-SO with MOLCAS 8.4.

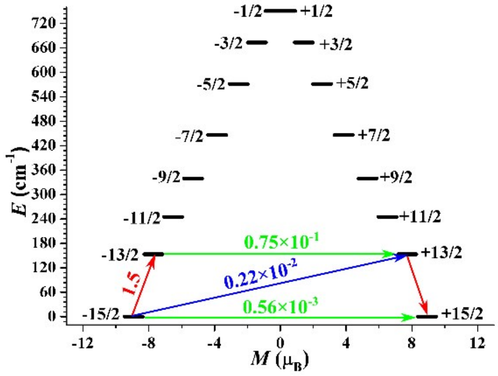
θ	E/cm^{-1}	wave functions
1.80 Å	0.0	90.39%|±15/2>+4.77%|±9/2>
	112.4	82.59%|±13/2>+12.70%|±11/2>
1.90 Å	0.0	97.91%|±15/2>
	142.4	96.79%|±13/2>
2.00 Å	0.0	99.40%|±15/2>
	153.9	99.07%|±13/2>
2.10 Å	0.0	99.58%|±15/2>
	152.5	99.35%|±13/2>
2.20 Å	0.0	99.75%|±15/2>
	145.9	99.61%|±13/2>
2.30 Å	0.0	99.84%|±15/2>
	136.6	99.74%|±13/2>
2.40 Å	0.0	99.89%|±15/2>
	126.6	99.81%|±13/2>
2.50 Å	0.0	99.92%|±15/2>
	116.6	99.85%|±13/2>
2.60 Å	0.0	99.93%|±15/2>
	107.2	99.87%|±13/2>
2.70 Å	0.0	99.94%|±15/2>
	98.6	99.89%|±13/2>



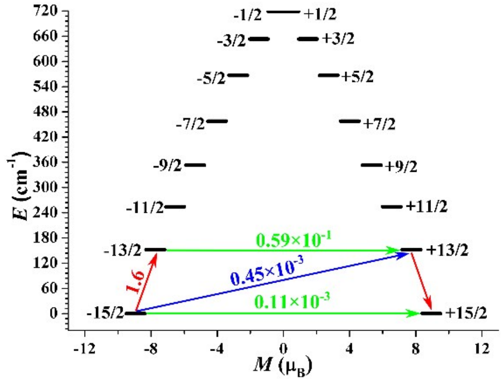
1.80 Å



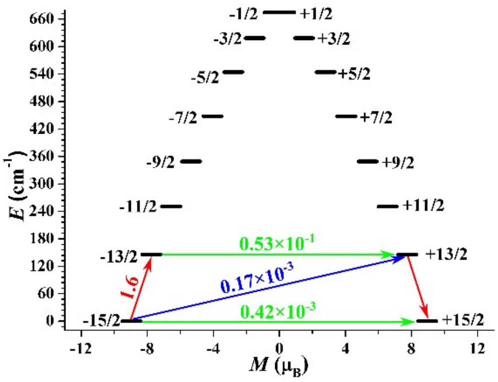
1.90 Å



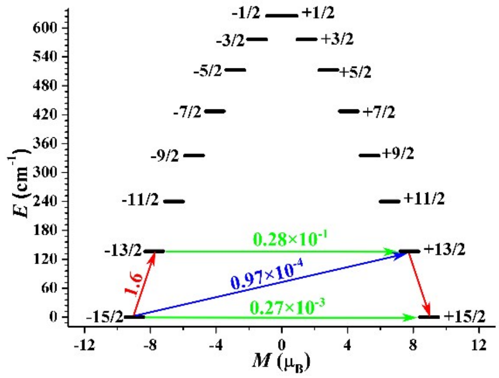
2.00 Å



2.10 Å



2.20 Å



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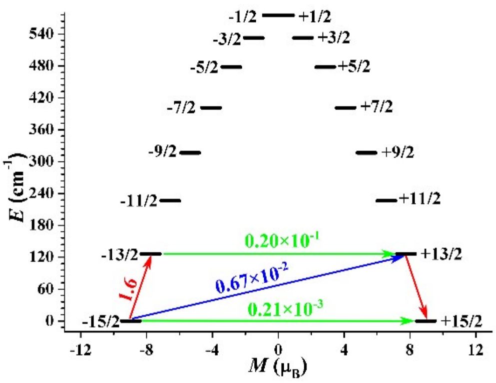
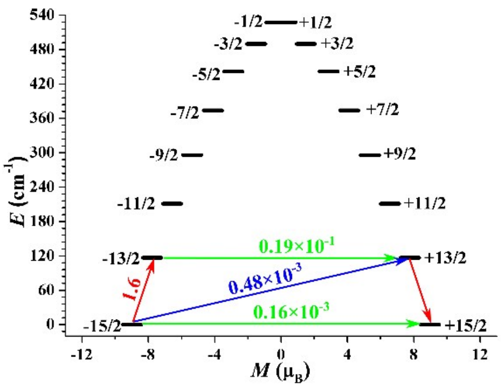
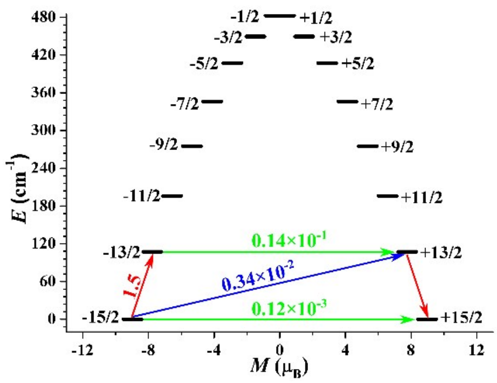
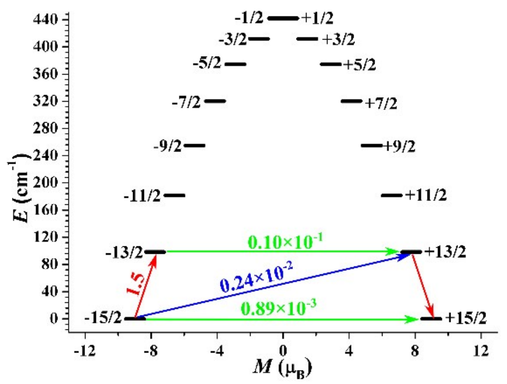


2.40 Å



2.50 Å





2.60 Å 2.70 Å

Figure S6. Magnetization blocking barriers for **2** with the different Er-O bond lengths keeping the θ of 90°. The thick black lines represent the KDs as a function of their magnetic moments along the magnetic axes. The green lines correspond to diagonal matrix elements of their transversal magnetic moments; the blue lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S14. Calculated energy levels (cm^{-1}), $\boldsymbol{g}$ (g_x, g_y, g_z) tensors and predominant m_J values of the lowest eight KDs of **3** with the different Er-C bond lengths (Å) keeping the θ of 90°using CASSCF/RASSI-SO with MOLCAS 8.4.

Er-C / KDs	1.80 Å			1.90 Å			2.00 Å		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.007 0.011 12.682	±15/2	0.0	0.000 0.001 17.291	±15/2	0.0	0.000 0.000 17.703	±15/2
2	44.0	7.586 7.573 3.491	±5/2	170.5	2.966 2.975 12.206	±13/2	215.2	0.992 0.994 14.956	±13/2
3	101.8	4.905 4.942 6.505	±9/2	207.7	2.408 2.409 10.845	±11/2	270.3	0.871 0.872 12.645	±11/2
4	130.2	0.017 0.025 10.803	±13/2	223.2	0.002 0.031 9.651	±9/2	306.1	0.001 0.020 10.096	±9/2
5	163.8	4.077 4.096 10.253	±11/2	250.4	6.900 6.838 5.782	±7/2	357.2	7.049 7.013 5.523	±7/2
6	310.4	7.487 7.471 2.703	±3/2	435.3	7.672 7.650 2.197	±3/2	532.7	7.136 7.120 2.914	±3/2
7	405.0	0.009 0.094 3.547	±7/2	519.8	0.007 0.089 2.779	±5/2	620.4	0.019 0.081 3.007	±5/2
8	469.6	8.954 8.875 1.372	±1/2	583.4	9.331 9.214 0.975	±1/2	683.5	9.478 9.351 1.013	±1/2
Er-C / KDs	2.10 Å			2.20 Å			2.30 Å		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.000 0.000 17.817	±15/2	0.0	0.000 0.000 17.868	±15/2	0.0	0.000 0.000 17.897	±15/2
2	229.1	0.533 0.534	±13/2	227.7	0.358 0.358	±13/2	218.5	0.260 0.261	±13/2

		15.284			15.387			15.437	
3	299.6	0.460 0.461 12.885	±11/2	308.2	0.303 0.305 12.964	±11/2	304.8	0.217 0.218 13.007	±11/2
4	349.2	0.000 0.015 10.266	±9/2	367.4	0.001 0.013 10.349	±9/2	370.3	0.002 0.011 10.408	±9/2
5	414.2	6.736 6.710 5.854	±7/2	439.4	6.488 6.467 6.084	±7/2	445.5	6.237 6.255 6.281	±7/2
6	582.0	6.746 6.736 3.366	±5/2	597.4	6.480 6.475 3.639	±5/2	591.5	6.243 6.241 3.856	±5/2
7	670.1	0.027 0.073 3.111	±3/2	682.6	0.033 0.068 3.170	±3/2	672.0	0.036 0.065 3.220	±3/2
8	731.1	9.532 9.406 1.055	±1/2	740.0	9.558 9.434 1.082	±1/2	725.1	9.574 9.452 1.102	±1/2
Er-C	2.40 Å			2.50 Å			2.60 Å		
KDs	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.000 0.000 17.914	±15/2	0.0	0.000 0.000 17.926	±15/2	0.0	0.000 0.000 17.934	±15/2
2	205.7	0.195 0.196 15.468	±13/2	191.7	0.149 0.149 15.489	±13/2	177.9	0.114 0.114 15.503	±13/2
3	295.0	0.160 0.161 13.037	±11/2	281.9	0.120 0.121 13.060	±11/2	267.6	0.090 0.091 13.078	±11/2
4	364.3	0.003 0.010 10.459	±9/2	353.3	0.003 0.009 10.504	±9/2	339.7	0.003 0.007 10.545	±9/2
5	440.4	5.993 6.008 6.473	±7/2	428.7	5.725 5.738 6.665	±7/2	413.6	5.434 5.445 6.857	±7/2
6	573.2	5.996 5.994 4.059	±5/2	548.5	5.727 5.725 4.258	±5/2	521.2	5.436 5.434 4.453	±5/2
7	648.5	0.039 0.063 3.267	±3/2	618.5	0.043 0.063 3.313	±3/2	586.1	0.044 0.061 3.355	±3/2
8	697.1	9.586 9.465	±1/2	662.7	9.596 9.475	±1/2	626.3	9.602 9.483	±1/2

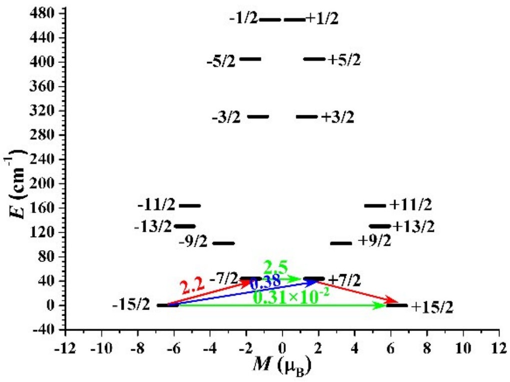
		1.117			1.130			1.141	

Er-C / KDs	2.70 Å		
	E/cm^{-1}	***g***	m_J
1	0.0	0.000 0.000 17.939	±15/2
2	164.9	0.087 0.087 15.515	±13/2
3	253.3	0.068 0.069 13.093	±11/2
4	325.1	0.003 0.006 10.580	±9/2
5	396.9	5.121 5.131 7.044	±7/2
6	493.6	5.123 5.121 4.643	±5/2
7	553.6	0.045 0.060 3.393	±3/2
8	590.1	9.608 9.490 1.150	±1/2

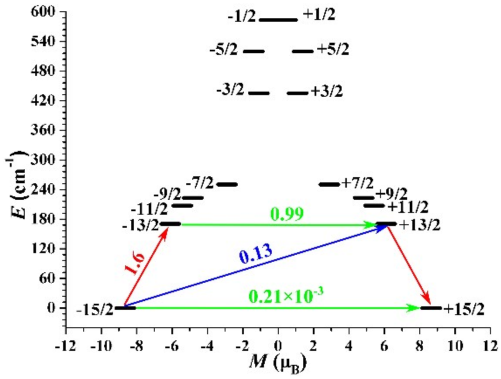
Table S15. Wave functions with definite projection of the total moments | m_J > for the lowest two KDs for **3** with the different Er-C bond lengths (Å) keeping the θ of 90° using CASSCF/RASSI-SO with MOLCAS 8.4.

θ	E/cm^{-1}	wave functions
1.80 Å	0.0	58.67%|±15/2>+41.64%|±9/2>
	44.0	11.27%|±13/2>+48.17%|±7/2>+28.29%|±5/2>+7.31%|±1/2>
1.90 Å	0.0	93.26%|±15/2>+6.39%|±9/2>
	170.5	77.23%|±13/2>+12.52%|±7/2>
2.00 Å	0.0	97.98%|±15/2>
	215.2	95.73%|±13/2>
2.10 Å	0.0	99.12%|±15/2>
	229.1	98.27%|±13/2>
2.20 Å	0.0	99.55%|±15/2>
	227.7	99.06%|±13/2>
2.30 Å	0.0	99.74%|±15/2>
	218.5	99.40%|±13/2>

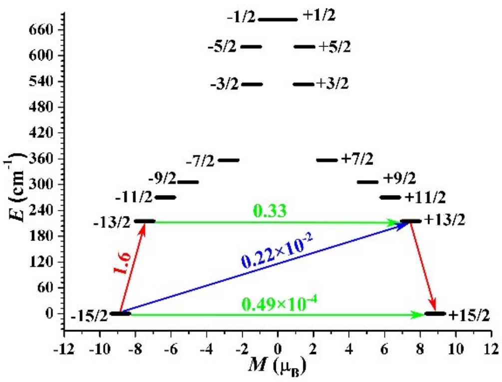
2.40 Å	0.0	99.84%|±15/2>
	205.7	99.59%|±13/2>
2.50 Å	0.0	99.89%|±15/2>
	191.7	99.70%|±13/2>
2.60 Å	0.0	99.92%|±15/2>
	177.9	99.77%|±13/2>
2.70 Å	0.0	99.94%|±15/2>
	164.9	99.82%|±13/2>



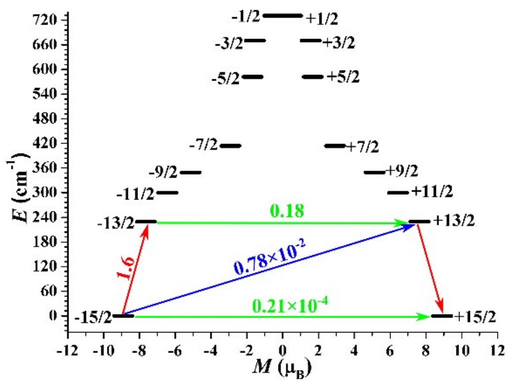
1.80 Å



1.90 Å



2.00 Å



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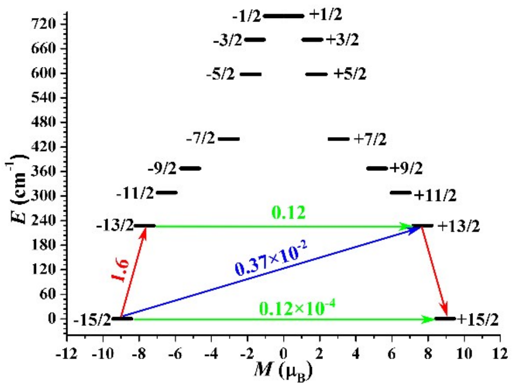

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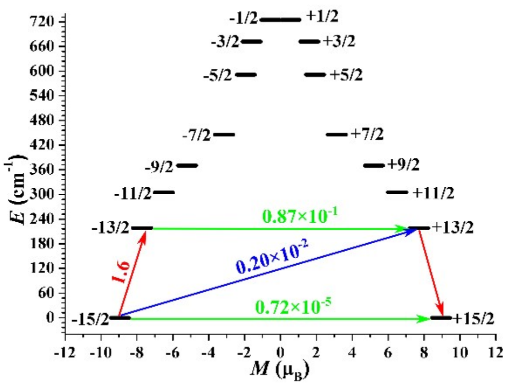

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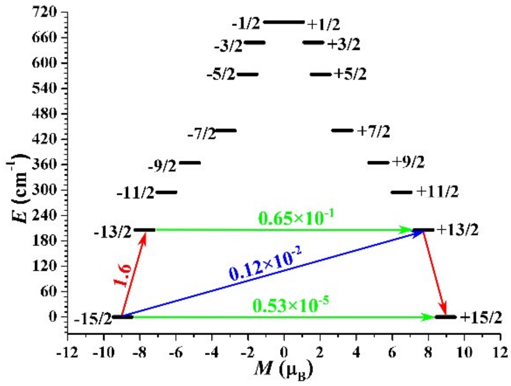

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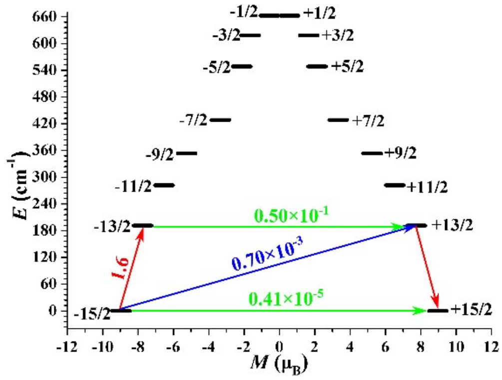

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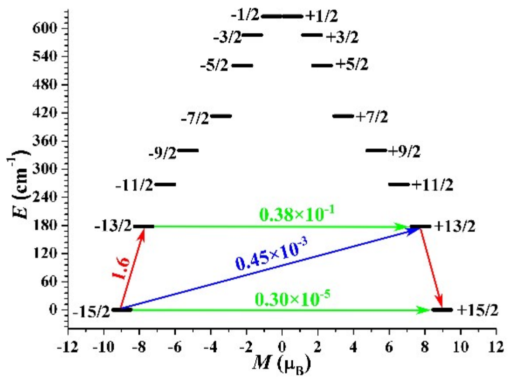

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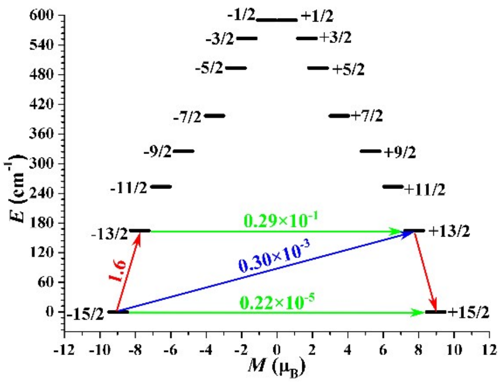


2.70 Å

Figure S7. Magnetization blocking barriers for **3** with the different Er-C bond lengths keeping the θ of 90°. The thick black lines represent the KDs as a function of their magnetic moments along the magnetic axes. The green lines correspond to diagonal matrix elements of their transversal magnetic moments; the blue lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S16. Calculated energy levels (cm^{-1}), ***g*** (g_x, g_y, g_z) tensors and predominant m_J values of the lowest eight KDs for simple model Er(NH_2)$_3$ with the different Er-N bond lengths (Å) keeping the θ of 90°using CASSCF/RASSI-SO with MOLCAS 8.4.

Er-N \ KDs	1.80 Å			1.90 Å			2.00 Å		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
1	0.0	1.871 5.114 12.143	±15/2	0.0	0.040 0.090 17.623	±15/2	0.0	0.006 0.012 17.801	±15/2
2	41.0	0.238 4.280 11.954	±13/2	162.9	1.315 4.829 12.982	±11/2	221.3	0.111 0.270 15.337	±13/2
3	78.3	5.286 3.059 0.704	±7/2	191.4	1.085 3.266 8.978	±9/2	261.9	1.171 1.381 11.924	±11/2

4	186.1	0.069 2.692 10.436	±9/2	260.4	2.120 5.233 9.356	±7/2	315.5	2.704 3.504 10.951	±9/2
5	352.1	0.580 1.333 14.926	±11/2	330.3	1.188 1.451 15.692	±13/2	375.2	3.068 3.890 11.907	±7/2
6	399.2	2.119 4.410 10.321	±3/2	512.7	2.556 4.637 10.044	±3/2	587.8	2.921 4.747 9.435	±5/2
7	555.6	0.017 2.934 6.596	±1/2	643.8	0.319 2.656 5.811	±5/2	701.3	0.474 2.756 5.153	±3/2
8	663.4	0.934 5.911 12.368	±5/2	739.7	0.926 6.222 12.321	±1/2	782.8	0.955 6.547 12.143	±1/2
Er-N	2.10 Å			2.20 Å			2.30 Å		
KDs	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
1	0.0	0.001 0.003 17.861	±15/2	0.0	0.000 0.001 17.892	±15/2	0.0	0.000 0.001 17.912	±15/2
2	224.2	0.335 0.455 15.353	±13/2	213.3	0.275 0.324 15.410	±13/2	199.3	0.197 0.219 15.453	±13/2
3	291.2	0.108 0.805 12.663	±11/2	297.6	0.048 0.471 12.867	±11/2	294.0	0.053 0.294 12.962	±11/2
4	348.2	2.002 2.534 10.290	±9/2	367.2	1.419 1.738 10.211	±9/2	372.7	1.020 1.213 10.312	±9/2
5	423.7	4.406 5.136 9.502	±7/2	449.2	4.956 5.688 8.285	±7/2	457.1	5.136 6.065 7.453	±7/2
6	618.1	3.217 4.801 8.894	±5/2	620.3	3.503 4.795 8.354	±5/2	606.3	3.791 4.731 7.792	±5/2
7	717.6	4.653 2.875 0.605	±3/2	708.4	4.280 2.986 0.778	±3/2	685.1	4.025 3.081 1.015	±3/2
8	787.0	12.008 6.778 0.987	±1/2	768.3	11.942 6.907 1.016	±1/2	737.3	11.956 6.933 1.037	±1/2
Er-N	2.40 Å			2.50 Å			2.60 Å		
KDs	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
1	0.0	0.000	±15/2	0.0	0.000	±15/2	0.0	0.000	±15/2

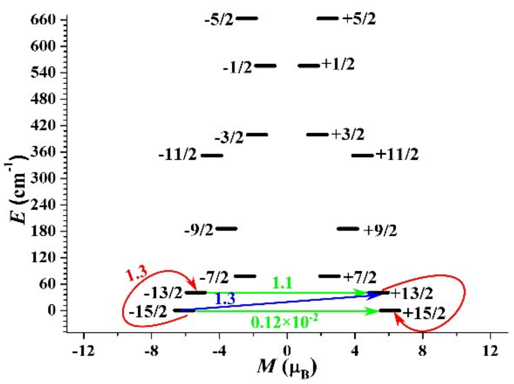
		0.001 17.924			0.000 17.933			0.000 17.940	
2	185.2	0.139 0.151 15.482	±13/2	172.0	0.100 0.106 15.501	±13/2	160.1	0.072 0.076 15.515	±13/2
3	285.2	0.041 0.194 13.018	±11/2	274.0	0.030 0.132 13.055	±11/2	261.8	0.022 0.093 13.081	±11/2
4	369.2	0.749 0.873 10.410	±9/2	360.1	0.563 0.645 10.489	±9/2	348.1	0.432 0.489 10.550	±9/2
5	453.6	6.844 6.316 5.106	±7/2	443.3	6.795 6.054 4.943	±7/2	429.1	4.693 5.537 7.021	±7/2
6	583.7	4.073 4.612 7.213	±5/2	557.3	4.315 4.468 6.625	±5/2	529.8	4.204 4.618 6.037	±5/2
7	654.9	3.869 3.160 1.300	±3/2	622.1	3.789 3.221 1.610	±3/2	589.0	3.763 3.268 1.928	±3/2
8	701.0	12.033 6.877 1.051	±1/2	663.2	12.152 6.763 1.058	±1/2	626.1	1.059 6.614 12.297	±1/2

Er-N / KDs	2.70 Å		
	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.000 0.000 17.944	±15/2
2	149.3	0.053 0.055 15.524	±13/2
3	249.4	0.016 0.066 13.099	±11/2
4	334.6	0.340 0.379 10.596	±9/2
5	412.9	4.391 5.030 7.243	±7/2
6	502.6	5.461 4.840 3.967	±5/2
7	557.1	3.771	±3/2

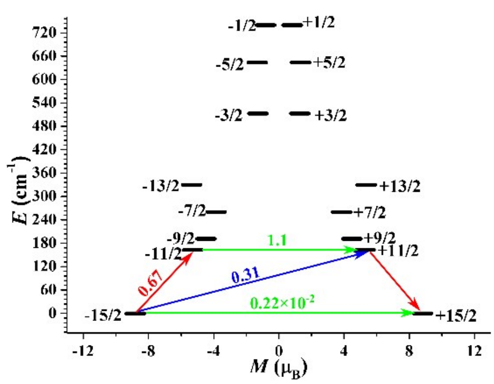
		3.302 2.234	
8	590.7	1.057 6.450 12.449	±1/2

Table S17. Wave functions with definite projection of the total moments | m_J > for the lowest two KDs for simple model Er(NH_2)$_3$ with the different Er-N bond lengths (Å) keeping the θ of 90° using CASSCF/RASSI-SO with MOLCAS 8.4.

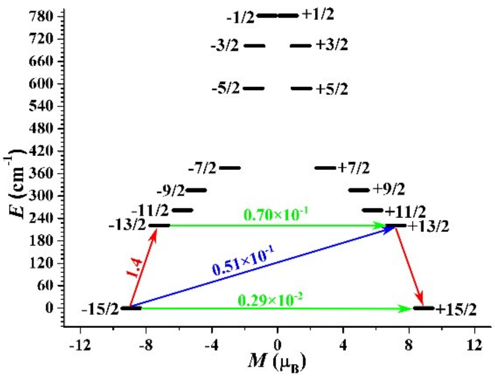
Er-N	*E*/cm^{-1}	wave functions
1.80 Å	0.0	60.43%|±15/2>+24.57%|±13/2>
	41.0	32.02%|±15/2>+26.43%|±13/2>+10.74%|±9/2>+10.85%|±7/2>
1.90 Å	0.0	98.10%|±15/2>
	162.9	14.94%|±13/2>+48.40%|±11/2>+22.97%|±9/2>
2.00 Å	0.0	99.47%|±15/2>
	221.3	73.59%|±13/2>+22.40%|±11/2>
2.10 Å	0.0	99.76%|±15/2>
	224.2	93.65%|±13/2>
2.20 Å	0.0	99.86%|±15/2>
	213.3	97.90%|±13/2>
2.30 Å	0.0	99.91%|±15/2>
	199.3	99.08%|±13/2>
2.40 Å	0.0	99.94%|±15/2>
	185.2	99.51%|±13/2>
2.50 Å	0.0	99.96%|±15/2>
	172.0	99.70%|±13/2>
2.60 Å	0.0	99.97%|±15/2>
	160.1	99.81%|±13/2>
2.70 Å	0.0	99.98%|±15/2>
	149.3	99.87%|±13/2>



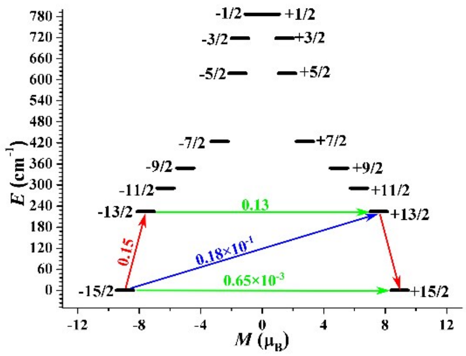
1.80 Å



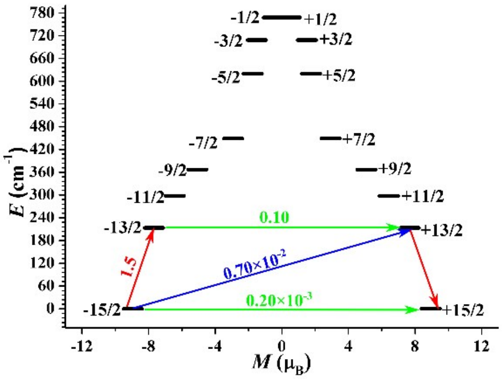
1.90 Å



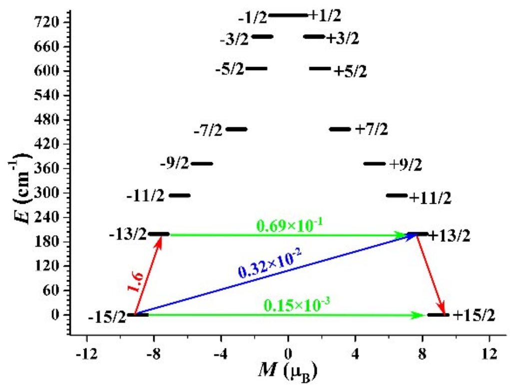
2.00 Å



2.10 Å



2.20 Å



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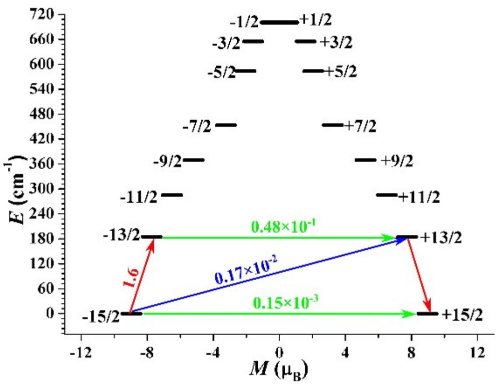
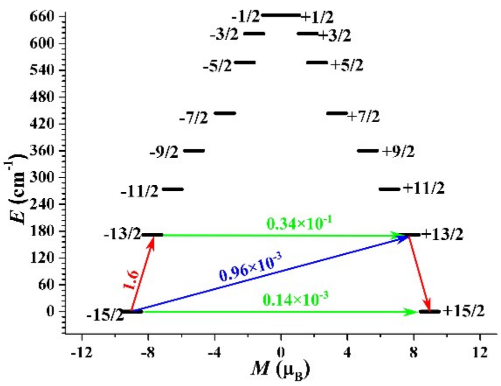
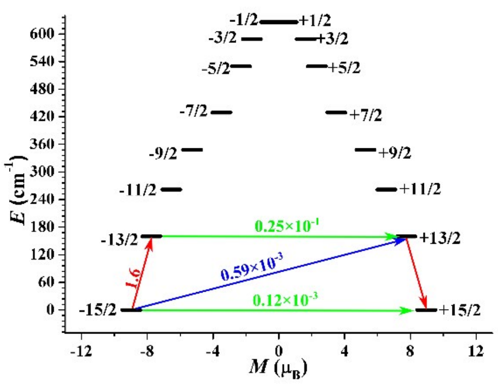


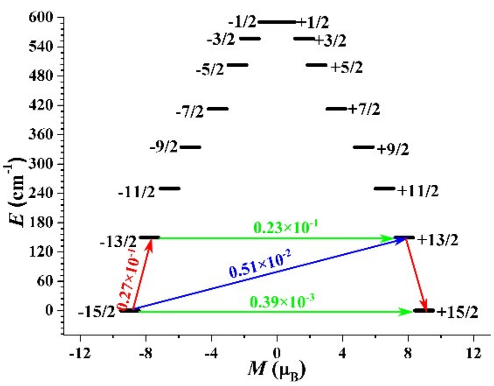
2.40 Å



2.50 Å



2.60 Å



2.70 Å

Figure S8. Magnetization blocking barriers for model $Er(NH_2)_3$ with the different Er-N bond lengths keeping the θ of 90°. The thick black lines represent the KDs as a function of their magnetic moments along the magnetic axes. The green lines correspond to diagonal matrix elements of their transversal magnetic moments; the blue lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.